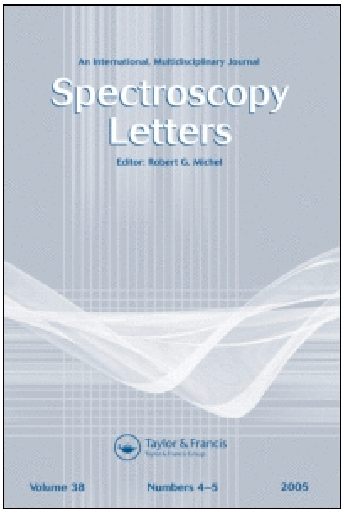

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Influence of Roughness Surfaces on Third-Order Nonlinear-Optical Properties of Erbium-Doped Zinc Oxide Thin Films

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ABSTRACT Zinc oxide (ZnO) and erbium-doped zinc oxide (ZnO:Er) thin films were deposited on heated glass substrates using the spray pyrolysis technique. Third-order nonlinear-optical properties of the thin films have been investigated using the third harmonic generation (THG) at wavelength of 1064 nm in picosecond regime. The dependence of third-order nonlinear susceptibility and transmission characteristics on the thin films roughness has been evaluated. Third-order nonlinear optical susceptibility ($\chi^{(3)}$) values of the studied materials were in the remarkable range of 10^{-2} esu. The morphologic properties of the deposited films have been analyzed using x-ray diffraction (XRD) and atomic force microscopy (AFM) and the luminescence properties by cathodoluminescence (CL). A correlation between optical properties and structural properties is given.

KEYWORDS spray, zinc oxide, nonlinear optical susceptibility, roughness surface

INTRODUCTION

Semiconductor oxide thin films are of considerable interest, due to their fast response time on laser excitation and large value of the third-order nonlinear susceptibility $\chi^{(3)}$[1] responsible for the Kerr effect. Optical nonlinearities of zinc oxide thin film were the subject of numbers of investigations.[2–4] The different influence of nanoparticle morphology (size and shape), preparation method (pulsed laser deposition,[5] RF magnetron sputtering,[6] molecular beam epitaxy,[7] etc.) together with laser radiation parameters (pulse duration, repetition rate, wavelength, etc.) on the nonlinear optical properties of this material were considered. However, surface roughness or rare earth doping effect has been rarely reported. Here, we report on the efficient third-harmonic generation (THG) in thin films of ZnO and ZnO:Er, prepared with spray pyrolysis, leading to direct generation of UV light from a Q-switched mode-locked Nd:YAG ($\lambda = 1064$ nm) laser.

Among the methods used for the investigation of nonlinear optical parameters of materials are the optical phase conjugation,[8], degenerate four-wave mixing (DFWM),[9] nonlinear interferometry,[10] the Z-scan technique,[11] and the THG.[12–14] Because of the high frequencies involved, the THG can probe purely coherent electronic nonlinearity. This technique also permits us to explore the absorption edge of the material without damaging the sample using the strong fundamental beam. One advantage of the THG technique is that the TH response accounts only for the ultrafast electronic response, so that vibrational, orientational, and thermal effects, which may contribute to the overall nonlinear response of the material, are excluded.

MATERIALS AND METHODS

The spray pyrolysis experimental set-up has been described elsewhere.[15] The thin films of ZnO and ZnO:Er were deposited from an aqueous solution containing zinc chloride ($ZnCl_2$) and ($ErCl_3$,Ù$6H_2O$). The glass substrates used are heated at three temperatures (400°C, 450°C, and 500°C). The spraying flow rate is set to 5 mL/min. The thin films were investigated using x-ray diffractometer (model XRG3000), profilometry, and atomic force microscopy. The atomic force microscope (DIGITAL Instruments) was equipped with a probe (OTR8 Veeco NanProb™). AFM images were acquired using the intermittent contact mode. The AFM measurements were performed in air. Surface areas were equal to 6.3*6.3 μm^2.

THG measurements (Fig. 1) were performed using a Q-switched mode-locked Nd:YAG ($\lambda = 1064$ nm) laser (model: Quantum elite) as the pump beam. It offers 1.62 mJ/pulse (pulse duration 15 ps) at 10 Hz. The fundamental beam energy was controlled with a polarizer and a half-wave plate then focalized on the sample through lens with forces of 25 cm. The beam diameter was 0.65 mm and the applied power density was 2 GW/cm^2. The sample was mounted on rotational step motor. A selective filter (at 355 nm) is used to absorb the pump beam allowing only the generated one to be collected in a photomultiplier tube (PMT). We also used density filters to reduce the generated intensity by the nonlinear medium. The third harmonic signal was detected by PMT (Hamamatsu), which was integrated with a boxcar and processed by a computer. A portion of the input beam was picked off and measured by fast photodiode to monitor the input energy. Finally we got the so-called Maker-fringes, which were generated by rotating the sample through the range from ±60 to the normal. Figure 2 shows Maker-fringes obtained for the fused silica taken as reference material to calibrate the experimental set-up and fitted with the chosen model given below[13]. The value of $\chi^{(3)}$ obtained for the fused silica is $\chi^{(3)} = 2.62 \times 10^{-4}$ esu.

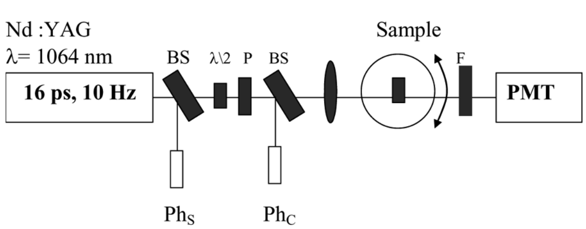

FIGURE 1 **THG experimental setup: Ph_S, synchronization photodiode; Ph_C, control photodiode; $\lambda/2$, half-wave plate; BS, beam splitter; P, polarizer; F, transmitting filter at 355 nm; PMT, photomultiplier tube.**

$$I_{3\omega} = \frac{576\pi^6}{n_{3\omega} n_\omega^3 \lambda_\omega^2 c^2} |\chi^{(3)}|^2 I_\omega^3 L^2 \frac{\sin^2(\Delta k L/2)}{(\Delta k L/2)^2},$$

where $\Delta k = \frac{6\pi}{\lambda_\omega}(n_{3\omega} - n_\omega)$,

n_ω and $n_{3\omega}$ are the refractive indices of the film at the fundamental frequency and the frequency of the TH, respectively, λ_ω is the wavelength of the fundamental radiation, L is the film thickness, $\chi^{(3)}$ is the nonlinear optical susceptibility of the film, Δk is the wave-vector mismatch between the fundamental and TH waves in a film, and I_ω is the power of the incident radiation.

RESULTS

Figure 3 shows AFM micrographs of ZnO grown respectively at 400°C, 450°C, and 500°C; these micrographs illustrate that the substrates are entirely covered with grains of different sizes, revealing that the smoothest surface is obtained at 450°C. At 400°C or 500°C, the obtained layers consist of an agglomeration of bigger grains that causes more important roughness. The difference of the roughness can affect the optical properties and is in its turn affected by the crystallinity of the layers; this is in good agreement with the XRD patterns shown in Fig. 4, where all the films have the same preferential orientation along the (002) plane. The well-crystallized layer (FWHM = 0.2349°) gives the smoothest surface and it corresponds with the sample elaborated at 450°C. This layer is almost covered with well-shaped grains, which predicts less scattering light due to the lack of grain boundaries.[17] In Fig. 5 are plotted the transmission spectra of the undoped layers elaborated at

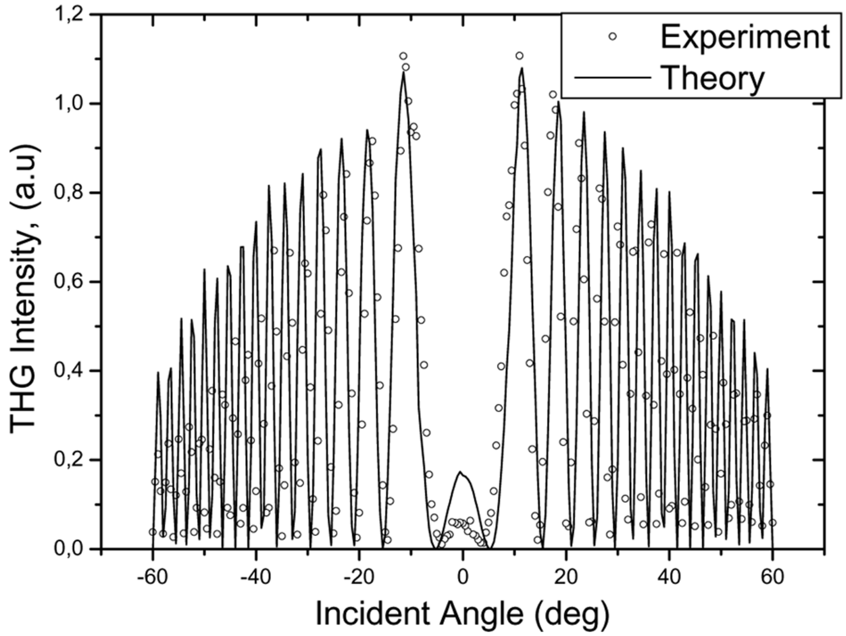

FIGURE 2 Theoretical and experimental Maker-fringes obtained on silica slab used as reference material.

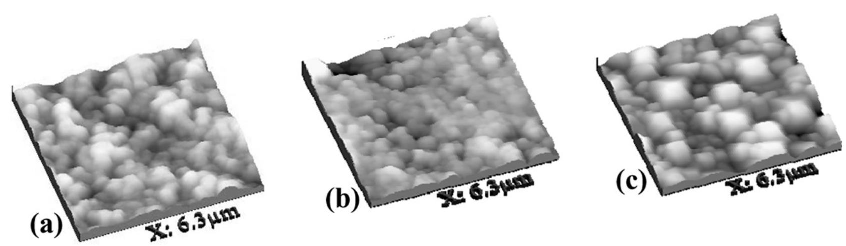

FIGURE 3 AFM micrographs of ZnO elaborated at different temperatures: (a) 400°C, (b) 450°C, and (c) 500°C.2

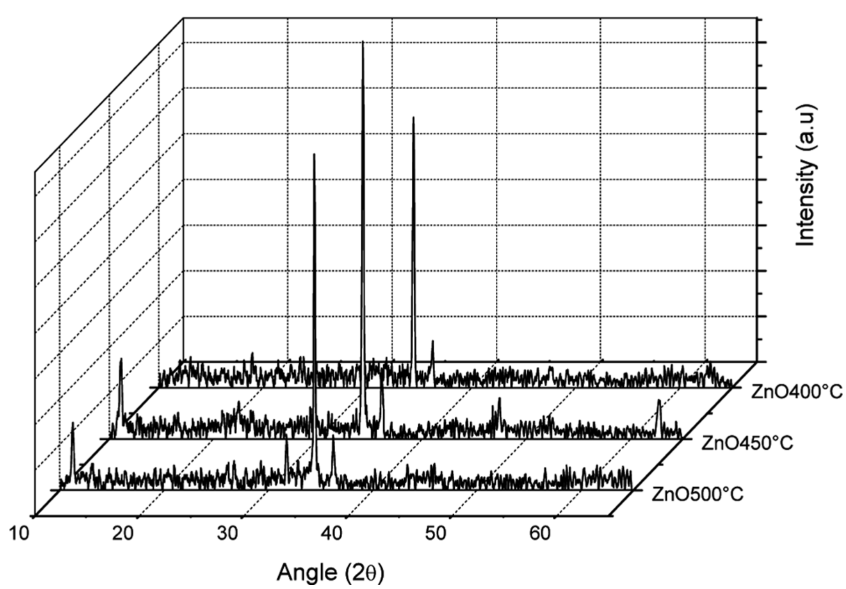

FIGURE 4 X-Ray diffraction patterns of undoped ZnO elaborated at different temperatures.

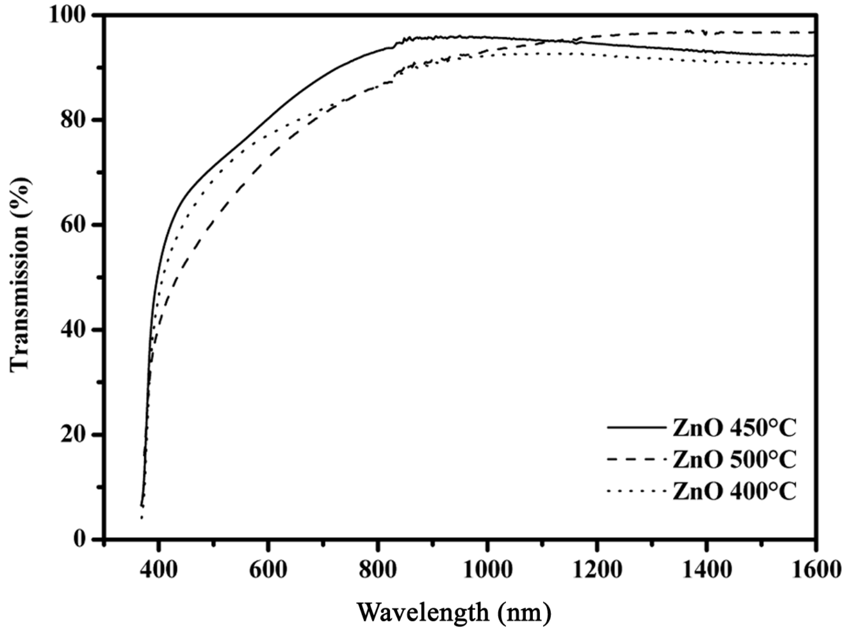

FIGURE 5 Transmission spectra of undoped ZnO elaborated at different temperatures.

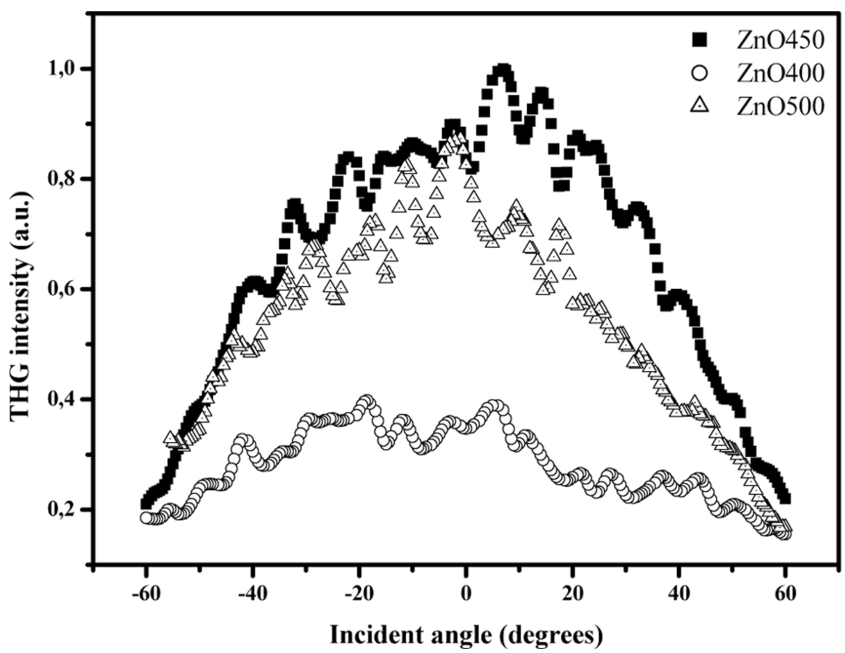

FIGURE 6 Normalized third-harmonic response of undoped ZnO given at three temperatures.

TABLE 1 Third-Order Nonlinear Susceptibility, RMS Roughness, and Thickness of Undoped ZnO and ZnO:Er 5% Elaborated at Different Temperatures

	Undoped ZnO			Er-doped ZnO		
Temperature of elaboration/(°C)	RMS (nm)	Thickness/ (nm)	$(\chi^{(3)} \pm 0.1) \times 10^{-12}$ [esu]	RMS (nm)	Thickness/ (nm)	$(\chi^{(3)} \pm 0.1) \times 10^{12}$ [esu]
4400	103	270	0,23	85	230	2,23
450	50	220	0,93	58	220	11
500	90	210	0,76	66	200	4,26

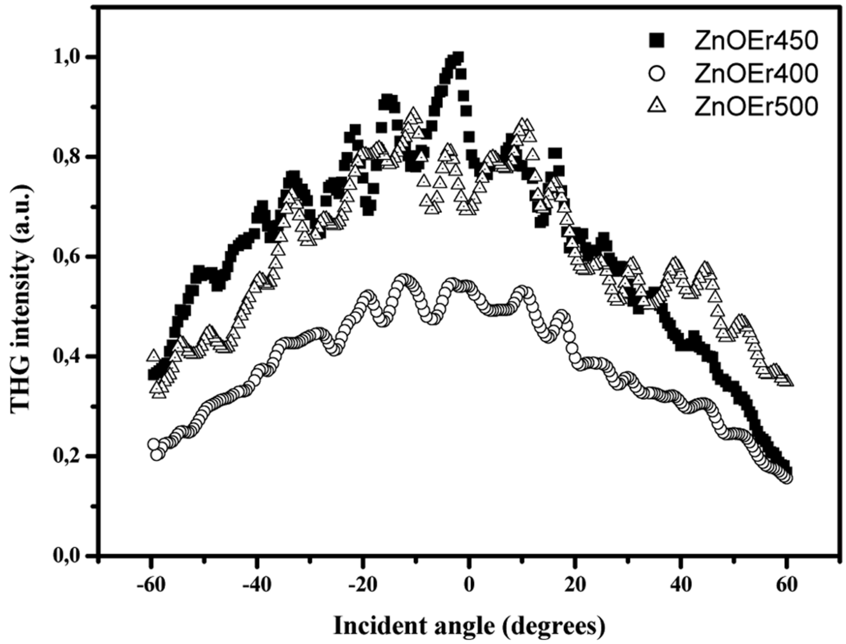

FIGURE 7 Normalized third-harmonic response of ZnO:Er 5% given at three temperatures.

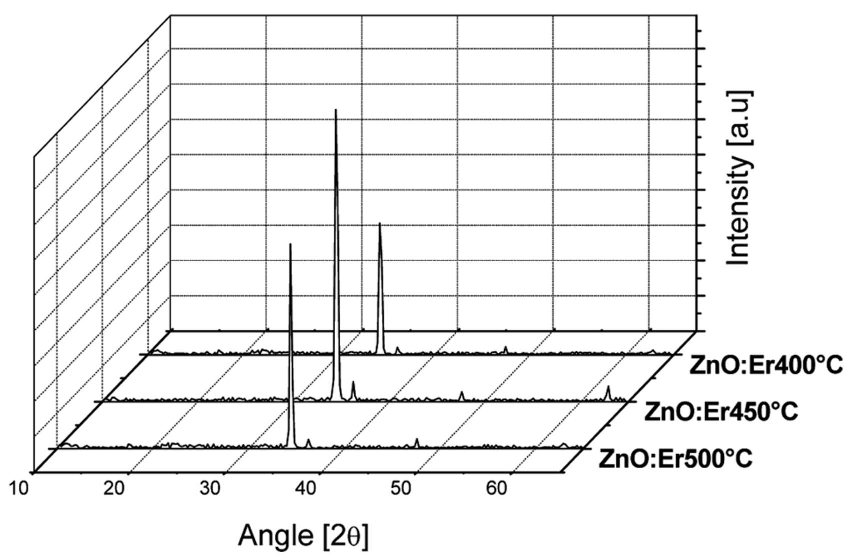

FIGURE 8 X-ray diffraction patterns of ZnO:Er 5% deposited at three substrate temperatures.

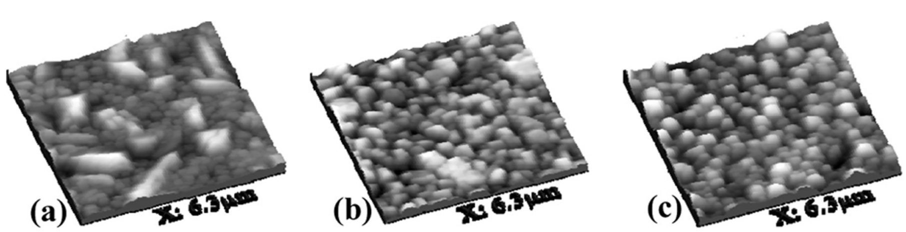

FIGURE 9 AFM micrographs of ZnO:Er 5% elaborated at different temperatures: (a) 400°C, (b) 450°C, and (c) 500°C.

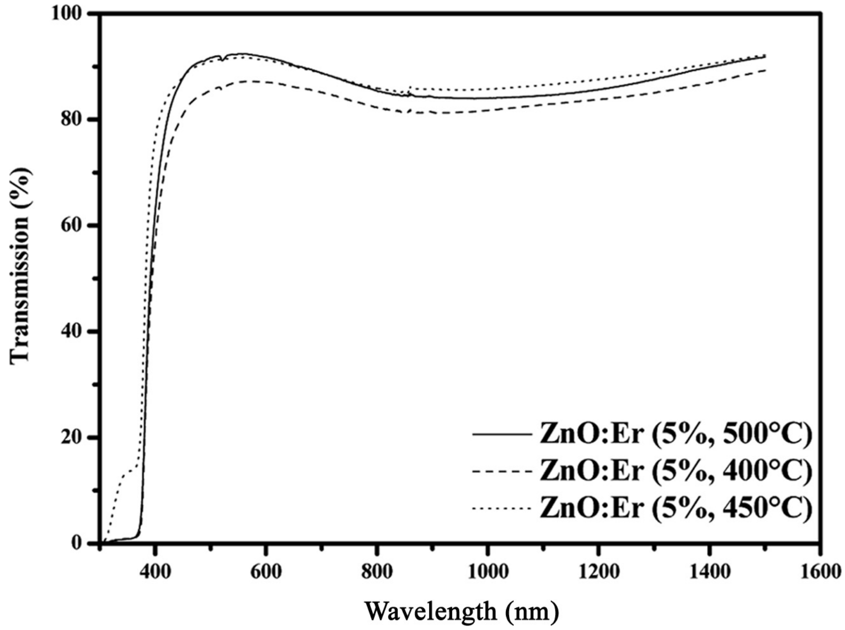

FIGURE 10 **Transmission spectra of ZnO:Er 5% elaborated at different temperatures.**

the three temperatures. It can be seen that all the films are transparent. The more important percentage of transparency is obtained for the smoothest layer, exceeding 80% in the visible region.

The transparency of ZnO at 1064 nm, which is the laser excitation wavelength, makes it a suitable candidate for nonlinear optical applications.[18] In fact, we have demonstrated that it has a good nonlinear response comparable with the ZnO layers fabricated by other techniques.[1] Figure 6 shows Maker-fringes obtained by rotating the sample through the range from ± 60 to the normal. The bell shape at the finges can be explained by the fact that the layer thickness is less important than its coherence length (generally of the order 1 μm). The calculated values from these spectra are given in Table 1. All the values are higher than the reference material. In order to improve the nonlinear susceptibility, we have used a rare earth as doping agent with an atomic concentration of 5%. The doped samples are elaborated in the same conditions. Erbium is believed to cause a substantial charge density redistribution within the crystalline ZnO:Er films[19] and offers extra free charge carriers and then may lead to higher $\chi^{(3)}$ values? by additional charge density polarization as it was already explained in our earlier work.[4] This work supports also previous results reported by Williams et al.[20] on erbium doping effect. It was demonstrated that third-order optical effect in ZnO:Er films is enhanced with increasing film thickness due to the disturbance of the long-range ordering in the nanocrystallites for the film with larger film thickness. Such effect may be explained due to Er ions creating additional local polarizability.

Effectively, in our experiments, the strongest THG signal was observed from the doped films especially the one elaborated at 450°C Fig. 7. This may be explained by two suggestions: one is the film crystallinity and the other is the surface roughness. From Fig. 8, all the films belong to the hexagonal wurtzite geometry, having the same peaks, but they differ as the roughness is concerned. Comparing the doped layers on Fig. 9, we find that that the sample elaborated at 450°C has relatively smooth surface which confirms the optical transmission results on Fig. 10. The smooth surface scatters less light from the fundamental beam and generates the highest nonlinear optical response.

CONCLUSION

Good-quality ZnO thin films have been elaborated using spray pyrolysis technique and their nonlinear optical properties investigated through third-harmonic generation by Maker fringes experiment. The results show a strong dependence of the third-order nonlinear susceptibility on the surface roughness but also on the sample crystallinity. The erbium doping has effectively improved the nonlinear response by introducing additional local polarizability; being itself dependent on the optical surface quality. In this study, we did not pay attention to the substrate, which may also contribute to the films crystallinity. The surface tension may play a major role in the film deposition as it was reported in a previous work[21] in which it was shown that the use of ITO buffer reduces the roughness.

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